THE LANTHANON CONTENT OF KING ISLAND SCHEELITE ORE*

By R. C. VICKERY†

The occurrence of lanthanons and their distribution in Swaziland scheelite was examined by Servigne (1940) and by Marsh (1943). Although these workers disagreed on the europium content of the ore they studied, the total lanthanon content observed (0.05 per cent. Ln_2O_3) was significant enough to warrant an examination of Australian scheelite for similar occurrences of lanthanons.

The initial scheelite investigated was from King Island and three samples were examined : (a) "run of mine" ore containing 0.6 per cent. CaWO₄, 10-20 per cent. CaCO₃, the balance being substantially andradite ; (b) a primary concentrate from the first flotation beneficiation of the "run of mine" ore containing 12-19 per cent. CaWO₄, the remainder being CaCO₃; (c) the final "sales" material containing 83 per cent. CaWO₄, balance CaCO₃. Lanthanons were found only in the original ore, sample (a), to the extent of 0.4 per cent. The oxide isolated contained a radioactive constituent, 20 ml of solution containing 0.17 g oxide gave 33 counts/min ($\beta + \gamma$ -radiation) above background. No radiation was observed from samples (b) or (c). These results suggested concentration of lanthanons and radioactivity in the primary flotation residues, and analysis of these residues gave 0.7 per cent. Ln₂O₃, and 0.2 g of oxide in 20 ml of solution gave 35 c/min above background.

Several accounts have been given of the geology and mineralogy of the King Island scheelite ore body and the most comprehensive mineragraphic report (Stillwell 1942) records the presence of more than 30 mineral species. The presence in the ore body of monazite or other lanthanon minerals was not reported and of the minerals observed only five have previously been reported as containing lanthanons : apatite, sphene, epidote, zoisite, and andradite. Garnets frequently contain lanthanons (Rankama and Sahama 1949; Jaffe 1951) but in such occurrences yttrium and the heavy lanthanons generally preponderate on account of their more suitable ionic size. Moreover, the occurrence of lanthanons is more to be expected in the spessartite garnets. Visual examination of the absorption spectrum of their solution showed the oxides derived from the flotation residues to be mainly light lanthanons and analysis of handpicked specimens of andradite showed no lanthanons therein.

Centrifugal separation of the flotation residue in methylene iodide (D:3.325) yielded an apatite concentrate (float) in which no lanthanons could be detected. Nitric acid treatment of the flotation residues, which could be expected to decompose and dissolve much of the apatite, likewise, showed no lanthanon extraction. The residual minerals, epidote and sphene, together with much andradite, were subjected to magnetic and electrostatic separations

* Manuscript received May 4, 1953.

[†] Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

SHORT COMMUNICATIONS

which yielded 60 per cent. concentrates of each of these minerals. Of the lanthanons originally present 80 per cent. was found in the epidote concentrate. Although allanite (orthite) is a common lanthanon epidote neither detection of its presence, nor determination of the mode of occurrence of the lanthanons in the epidote was directly possible. Solutions of the epidote concentrate were radioactive but less so than a solution of New South Wales monazite containing the same amount of lanthanon oxides. Percentage distribution of extracted lanthanons in terms of the oxides was:

Ce 39.2; Pr 13.1; Nd 26.1; Sm 4.8; Eu 0.85.

No indications of the presence of dysprosium or erbium were found, and the balance of the oxides was probably lanthana since basicity separation in fused ammonium nitrate (Vickery 1949) yielded a lanthanum concentrate equivalent to $14 \cdot 2$ per cent. La₂O₃. Due to background absorption, the spectrophotometrically determined value for europium is likely to be some 5 per cent. too high. The ratios of elements generally are similar to those expected for allanite or monazite (Rankama and Sahama loc. cit.) although the Nd : Pr ratio is somewhat lower than usual and even deducting 5 per cent. from the europium value the Eu : Sm ratio is much higher than normally encountered in allanite or monazite. Such an increase in the Eu : Sm ratio was also observed by Marsh (loc. cit.) working on the Swaziland ore.

Experimental

Of each of the original samples (a), (b), and (c) 200 g was decomposed in aliquots by fusion with sodium peroxide. The cooled mass was extracted with water and the residue washed free from alkali before dissolution in 50% HNO₈. Several alternate precipitations as hydroxide and oxalate were necessary for adequate removal of calcium and iron. In the presence of much iron, precipitation of lanthanon oxalates is always somewhat inhibited, and in some cases standing for a week was necessary to obtain precipitation of the lanthanon oxalates from the highly ferruginous solution.

Radioactivity was measured through an A.E.L. type SC100-1 instrument with counting periods of 3 hr or longer.

The methylene iodide separations were effected by centrifuging at 2500 r.p.m. in waterbuffered tubes.

Spectrophotometric analysis of the final oxides was carried out on the Beckmann DU instrument utilizing the absorption wavelengths and extinction coefficients given by Moeller and Brantley (1950) the appropriate corrections being applied for interfering ions.

The author's thanks are due to Mr. E. S. Pilkington for carrying out check analyses of the ore samples, and to Dr. R. Segnit and Mr. A. J. Gaskin for helpful advice on minerals separation and for carrying out the magnetic and electrostatic separations.

References

JAFFE, H. W. (1951).-Amer. Min. 36: 133.

MARSH, J. K. (1943).-J. Chem. Soc. 1943: 577.

MOELLER, T., and BRANTLEY, J. C. (1950).-Analyt. Chem. 22: 433.

RANKAMA, K., and SAHAMA, TH. (1949).—" Geochemistry." p. 524. (Chicago Univ. Press.) SERVIGNE, M. (1940).—C.R. Acad. Sci. Paris, **210**: 440.

STILLWELL, F. L. (1942).—Coun. Sci. Industr. Res. Aust. and Melbourne Univ. Mineragr. Rep. No. 251.

VICKERY, R. C. (1949).-J. Chem. Soc. 1949: 2508.